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INPUTS OF PHOSPHORUS FROM PRECIPITATION TO LAKE MICHIGAN

T. J. Murphy, et al

De Paul University

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Precipitation samples were collected at six locations around Lake Michigan and analyzed for the different forms of phosphorus present. It was found that the atmosphere is presently contributing one million kilograms per year of phosphorus or about 18 percent of the phosphorus budget of the Lake. As the phosphorus removal program on sewage effluents becomes fully implemented in the Lake Michigan basin, the contribution to the Lake of phosphorus from particulate matter scavenged by precipitation could increase to about 30 percent of the total.

The phosphorus concentration of precipitation was found to be higher at the southern end of the Lake. More than 40 percent of the phosphorus in precipitation is dissolved reactive phosphates and the amount of the dissolved phosphates in precipitation was found to be somewhat dependent on the pH of the sample.

The washout ratio for phosphorus by precipitation was determined. It was also found from the analysis of some glacial samples that phosphorus has long been a conponent of precipitation.

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INPUTS OF PHOSPHORUS FROM PRECIPITATION TO LAKE MICHIGAN

by

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ABSTRACT

Precipitation samples were collected at six locations around Lake Michigan and analyzed for the different forms of phosphorus present. It was found that the atmosphere is presently contributing one million kilograms per year of phosphorus or about 18 percent of the phosphorus budget of the Lake. As the phosphorus removal program on sewage effluents becomes fully implemented in the Lake Michigan basin, the contribution to the Lake of phosphorus from particulate matter scavenged by precipitation could increase to about 30 percent of the total.

The phosphorus concentration of precipitation was found to be higher at the southern end of the Lake. More than 40 percent of the phosphorus in precipitation is dissolved reactive phosphates and the amount of the dissolved reactive phosphates in precipitation was found to be somewhat dependent on the pH of the sample.

The washout ratio for phosphorus by precipitation was determined. It was also found from the analysis of some glacial samples that phosphorus has long been a component of precipitation.

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SECTION I

CONCLUSIONS

One million kilograms per year of phosphorus is being brought into Lake Michigan each year by precipitation scavenging. This is a significant factor in the phosphorus budget of the Lake.

The average concentration of phosphorus in precipitation is three times the 0.008 mg/l. concentration of phosphorus in the Lake. About half of the phosphorus in precipitation is in the form of dissolved reactive phosphates and thus should be immediately available to the organisms in the Lake.

That the concentration of phosphorus in precipitation is higher at the southern end of the Lake than at the northern end.

That the pH of the precipitation can affect the amount of dissolved reactive phosphates in precipitation.

That there has been phosphorus in precipitation in the northern hemisphere for at least the last three centuries.

SECTION II

RECOMMENDATIONS

That measurements of the phosphorus concentration in precipitation over the Lake be made.

That phosphorus inputs to Lake Michigan from dry fallout be determined.

That a pH be stipulated for the equilibrium of precipitation samples before filtration for the dissolved reactive phosphates determination.

SECTION III

INTRODUCTION

This project had as its primary objective the determination of the magnitude of phosphorus inputs to Lake Michigan in precipitation and to determine the form in which this phosphorus is present in precipitation. Other objectives were to determine the distribution of phosphorus in precipitation around the Lake, to develop indirect methods of estimating the precipitation inputs and to see if it could be determined whether the inputs via this route had changed through time.

Lake Michigan is the second largest by volume of the Great Lakes and the only one of the Great Lakes entirely within the United States. It has enormous value for sport and commercial fishing, for shipping, as a recreational area and as a source of fresh water supplies for industrial and municipal uses. It is still considered to be in an oligotrophic state although some areas show serious signs of degradation. In recent years a number of studies have shown that phosphorus is the principal limiting nutrient in the Lake (Miller, 1974; Schelske et al., 1974). There are indications that the phosphorus concentrations in the Lake are increasing (Vaughn, 1974; Lee, 1974). This presumably is the cause for the observed increases in the number of algal cells and changes in the species of algae in the Lake in recent years (Schelske et al., 1972; Stoermer, 1974). Because of the changing conditions in the Lake and the indications that phosphorus inputs are the cause, controls on the discharge of phosphorus in sewage effluents to the Lake or its tributaries were put into effect starting in 1973. In order to be able to evaluate the effect of this program and to formulate subsequent programs, the phosphorus budget of the Lake must be known. A determination of the phosphorus inputs to the Lake from tributaries and direct discharges in 1971 was made by the U. S. Environmental Protection Agency (1974). To date, no determination of inputs of phosphorus from precipitation have been made.

Inputs of nutrients in precipitation are a component of the nutrient budget of bodies of water. These inputs should be most significant in those cases where the lake is oligotrophic and occupies a significant portion of its drainage basin. This is true of Lake Michigan which occupies one third of its drainage basin, receives half of its water budget directly from precipitation, is relatively deep and has a hydraulic residence time greater than 100 years.

The chemical form of the phosphorus entering the Lake in precipitation is important since organisms utilize the phosphorus primarily in the form of ortho phosphate. Not all of the phosphorus entering the Lake can become available as ortho phosphate. Thus ortho phosphate and phosphates which can be hydrolyzed to ortho phosphate in the Lake are important while phosphorus which is strongly bound in organic or

inorganic compounds may never become available as ortho phosphate and therefore has no effect on the biota of the Lake. Most of the phosphorus present in eroded materials and much of the phosphorus discharged to tributaries far from the Lake is thought not to become available as ortho phosphate in the Lake.

To carry out this project, the following plan was developed. Precipitation samples would be collected in several locations around the Lake. These samples would be analyzed for the different forms of phosphorus present and the inputs of the different forms to the Lake would be calculated from the concentrations and the amount of precipitation. These inputs would be compared to inputs of phosphorus to the Lake from other sources.

The washout ratio for phosphorus containing particulate matter would be determined. The washout ratio is the ratio of the phosphorus in precipitation to the amount of phosphorus in the atmosphere. Knowing this ratio would permit the estimation of the phosphorus concentration in precipitation by the determination of the particulate phosphorus concentration in the atmosphere. Since high volume air particulate samples are routinely collected in many areas, this indirect method of determining phosphorus inputs could have wide applicability to present and historical samples. Finally, a series of glacial samples collected in Greenland was obtained. It was hoped that the analysis of these samples would indicate whether the concentration of phosphorus in the atmosphere had changed over time and, if so, by what factor.

SECTION IV

EXPERIMENTAL DESIGN

COLLECTION

Most atmospheric sampling has been of bulk precipitation. That is, both wet and dry fallout were collected. The problem with this is that it does not differentiate between the wet and dry inputs. This can be important because the particulate matter deposited by these two different routes can be very different in origin and composition. It was decided that the project would concentrate on the determination of the precipitation input component of the atmospheric loading. This was for several reasons. The first is that the dry fallout component is chiefly of particles larger than 20 micrometers, giant size aerosols. These have short atmospheric residence times and impact on the surface close to their source and therefore would be of only local significance. They still, however, could be of importance to the phosphorus budget and may contribute to the increased concentration of nutrients observed in the inshore waters of the Lake. The size distribution studies of particulate matter (Lee and Patterson, 1969; Cunningham et al., 1974) show that the phosphorus is present chiefly on aerosols with a mean diameter of a few micrometers. Thus, these particules will have a long atmospheric residence time and will be removed from the atmosphere chiefly by precipitation scavenging. To the extent that precipitation is uniform on the surface of the Lake, the inputs determined close to the shore should be a good approximation of the input on the surface of the Lake.

Trying to collect just wet fallout samples presented a number of problems. Ideally, the collector would be exposed only during the precipitation event to minimize the collection of dry fallout. Because of the activity of microorganisms in the samples, the samples would have to be collected and then immediately analysed or preserved for later analysis if the different forms of phosphorus present were to be accurately determined.

In order to collect the samples, people who lived or worked in the areas where sampling was desired and who were willing to help with the project were located. These people were asked to put out a clean collector each day, or on days when rain was anticipated, and to take in the sample after the precipitation event or, if no precipitation had fallen, to change collectors within 24 hours. It was realized that these people could not be expected to go very far out of their way on a regular basis to change the collectors and handle the samples for this project and so a suitable sampling location was found where it would be convenient for the person doing the sampling.

The washout ratio was determined by sampling the air before and/or during precipitation events to determine the phosphorus concentration

in the air and then dividing the phosphorus concentration found in the precipitation by this number.

Finally, glacial samples from Greenland were obtained from the U. S. Army's Cold Region Research and Engineering Laboratory (CRREL). The samples had been collected in an isolated area where snow continually deposits but where little or no melting occurs. Hence, non-volatile material deposited with the precipitation accumulates and leaves a permanent record with each years accumulation of snow. Samples of snow deposited approximately in the years 1270, 1650 and 1966 were obtained. These were analysed for the different forms of phosphates to see if it could be determined if the phosphorus concentration in the atmosphere had changed through time.

LOCATION

Six sampling locations were used for the project. The first of these was located on the roof of the science building at DePaul University in Chicago. The building (41° 55.4'N; 87° 39.3'W) was in a densely populated urban area about five km north of the central business area of Chicago and about two km west of the shore of the Lake. There was light manufacturing in the immediate vicinity. The roof was about fifteen meters above street level. The location of the collector on the roof undoubtedly decreased the number of traffic related aerosol particles incorporated in the samples. Also, it was above the normal habitat of insects and birds in the area and no problems with contamination from these sources were encountered during the project.

A second sampler in the Chicago area was located at the Harrison water intake crib of the City of Chicago (41° 55'N; 87° 34'W). This crib is located about four km from the west shore of Lake Michigan, just east of the City of Chicago. It is manned 24 hours a day by a caretaker and maintenance crew of 3-4 men. This station was chosen in order to obtain samples in the Chicago area at a location where it was anticipated that local inputs would be at a minimum. It was hoped that bias in the DePaul samples due to very local inputs would be discernable when compared to the samples collected at the crib.

The third collection site was located at Illinois Beach State Park, about 75 km north of Chicago along the Lake. The sampler was placed in an open area about 100 m from the shore (42° 26'N; 88° 48'W). The Park extends along the shore for about six km and is about 1.5 km deep. Beyond the Park on the west is a suburban area with light manufacturing. Five km to the south of the collection site is a large coal fired power plant and a nuclear power plant is located two km to the north. There is a resort motel and the maintenance buildings for the park in the vicinity of the sampling site.

The fourth collection site was located at Rock Island State Park (45° 25'N; 86° 49'W), an island maintained as a wilderness to the north of the Door Peninsula of Wisconsin. This site was about one km from the

nea: est inhabited area, a large island with a farming and fishing community, and more than 30 km from the nearest cities and industrial centers. The park superintendant did the collecting. Since the prevailing winds are from the west, it was hoped that this site would give information on the phosphorus in precipitation coming over the Lake in the northern part of the lake away from the population and industrial centers.

The fifth collection site was located on Beaver Island, the largest island in Lake Michigan. The island is located in the northern part of the Lake about 20 km from the nearest shore. It has an area of about 140 km^2 and a permanent population of about 200 people. Its industries are hunting, tourism and commercial fishing. The island is in a natural state witn much of it covered with forests. Only one farm is being worked on the island. The sampler was located in an open area about 0.5 km from the center of town in the northeast corner of the island (45° 45'N; 85° 31'W). The forest conservation officer who did the sampling for the project has been a cooperative weather observer for the National Weather Service for a number of years. This was an extremely useful sampling site for the project as it was the closest approximation arrived at for a sampling site in mid-Lake. With prevailing westerly winds, the air masses pass over more than 60 km of open water before getting to Beaver Island. The Beaver Island samples should be lower in concentration than any samples collected around the shores for two reasons. First, it is far from the inputs from the industrialized regions of the Lake and, secondly, being far from any shore some of the particulate matter has been scavenged by the time those air masses reach Beaver Island.

The last sampling site was at Silver Lake State Park along the east side of the Lake at a place where the land juts out into the Lake (43° 37'N; 86° 36'W). The area is rural with fruit the main crop. This site was expected to give information on the phosphorus concentration of air masses after they had passed over the Lake. The park superintendant did the sampling for the project.

The glacial samples were from ice cores taken at Camp Century in Greenland (77° 10'N; 61° 08'W).

The samplers were located in open areas and as far from roads as possible. But since these collectors had to be located near the home or office of the volunteers, there could be a problem with dust from roads and other local sources. This problem is minimized by the fact that the collectors are exposed only during precipitation events when the raising of dust from roads should be at a minimum.

Polyethylene buckets 25 cm high and with an opening 20 cm in diameter were used for the collectors. These were free of leachable materials and were easily cleaned and shipped. A holder was constructed which raised the bucket about a meter to prevent splash from the ground from getting into the collector. An adjacent rain gage was used to measure

precipitation. No attempt was made to collect all precipitation events although as many as possible were collected.

Precipitation samples collected in Chicago were brought in as soon as practical after the event, the pH of the sample was determined, the sample was placed in a polyethylene bottle and frozen.

Samples collected at the other locations were brought in by the participants as soon as practical, preserved with mercuric chloride (40 mg/l) and sodium chloride (50 mg/l), placed in a polyethylene bottle and mailed to Chicago. All necessary containers, boxes, labels, funnels, holders, etc. were supplied to the participants. Buckets were to be used only once and then returned to Chicago to be cleaned. This was to keep the participants from having to clean the buckets, but also to avoid problems with contamination with detergents and from buckets being used multiple times between cleanings, etc. A quantity of buckets was supplied such that an accumulation of 25 or so could be made before it was necessary that they be returned.

Evaporation of the sample after the precipitation event but before the sample is collected would concentrate the sample and lead to high estimates of the inputs. To correct for this, the participants were requested to return all of sample that was in the collector. From the amount of rain which fell and knowing the area of the collector, 300 cm^2, the amount of sample which should have been in the collector could be calculated. Any difference between this amount and the amount actually returned was assumed to have evaporated and was corrected for.

ANALYSIS

The basic analytical procedure used for phosphorus determinations was the single reagent method of the EPA (1971). A Bausch and Lomb spectrophotometer with a 2.5 cm path length sample tube was used for most analyses. The glacial samples and some other samples of low concentration, were analysed using a Beckman DK-2 recording spectrophotometer with a ten cm pathlength cell. Total reactive phosphates (TRP) analyses were done on unfiltered 12.5 ml samples. Dissolved reactive phosphates (DRP) determinations were done on 12.5 ml samples which had been filtered through a 0.45 nm cellulose nitrate (Sartorius 113 06) membrane filter. These membrane filters have been reported to be free of extractable phosphorus. This was checked on several occasions and no extractable phosphorus was found. Hydrolyzable phosphorus was determined on 25 ml samples digested with 0.5 ml of 11 N sulfuric acid. Total phosphorus was determined on 25 or 50 ml samples digested with ammonium persulfate (0.4 gm/50 ml) and sulfuric acid (11 N, 1.0 ml/50 ml). When possible, total phosphorus and total and dissolved reactive phosphates analyses were run in duplicate on all samples. When insufficient sample was available for all of the analyses, only total and/or dissolved reactive phosphates analyses were run.

A set of standards using ortho phosphate was run each day. The results from these analyses were used to determine the constants for a linear equation which related the absorbance of the samples to their phosphorus

concentration. When total phosphorus was determined, two or more phosphorus standards were run in addition to the ortho standards. To determine the relationship between the absorbance and the concentrations for the total phosphorus samples, it was assumed that the slope of the line was the same for both the ortho and total samples but that the intercept could be different. The total phosphorus standards were used to determine a new intercept for the correlation line.

The pH of the samples collected in Chicago was measured with a pH meter immediately after the sample was collected. The meter was standardized before use with a 0.05 molar solution of potassium acid phthalate. This is an NBS certified buffer, is readily prepared, is at a convenient pH (4.00 at 20°) and contains no phosphorus.

The concentration of the forms of phosphorus found in each sample and the amount of precipitation that the sample represented were used to calculate an input in kg/km^2 of the different forms of phosphorus in that sample. The summary results from a group of samples include some of the amounts of precipitation and inputs in kg/km^2, and a precipitation weighted average concentration is calculated by multiplying the concentration of phosphorus in mg/l. by the amount (cm) of precipitation and converting these units ($mg/1000\ cm^2$) to kg/km^2 by multiplying by 10. This gives the input of phosphorus for each sample. The average concentration then was determined by summing the inputs for each sample, dividing this total by the total amount of precipitation for those samples and multiplying by 0.1 to give the concentration in mg/l. This should be equivalent to the concentration that one would find if a sampler were placed out for the entire period, no evaporation occurred and the sample was collected at the end of the period, mixed well and analyzed.

The glacial samples were analyzed with the same reagents and under the same conditions as were used for the other samples. A 10 cm pathlength absorption cell was used for the measurements and an absorption spectrum of each sample, blank and standard was run from 600 nm to 950 nm. The absorption peak at 880 nm was used to calculate the phosphorus concentration.

Two of the glacial samples had a large absorption at 750 nm which obscurred the phosphorus absorption. Attempts were made to extract the phosphorus-molybdate complex from these samples but all the methods used (Isaeva, 1969; Goings and Eisenreich, 1974; Pakalns, 1972) gave high and variable blanks with the phosphorus concentrations of about one ppb.

Arsenate forms a similar complex to the phosphate under the conditions used for analysis and its absorption maximum is at 865 nm. This then is a possible interference in the phosphorus analysis. To check the possible magnitude of this interference, a number of precipitation samples were analyzed for arsenate by the method of Johnson (1971).

SECTION V

RESULTS

The weighted average concentration of phosphorus in the forms of total phosphorus and total and dissolved reactive phosphates for the precipitation samples collected in different regions of Lake Michigan are shown on Tables 1, 2 and 3. Included is information on the average amount of precipitation per sample, the average time the collector was exposed and statistical information. In addition the geometric mean concentration of the total phosphorus and dissolved reactive phosphate samples collected at DePaul was .0344 and .015. The distribution around the Lake of the phosphorus concentrations shown on Tables 1, 2 and 3 is shown in Figure 1.

Table 1. TOTAL PHOSPHORUS IN PRECIPITATION

	DePaul Univ.	Beaver Island	Silver Lake	Illinois Beach	Rock Island	Harrison Crib
Total Precipitation (cm)	101.7	19.5	33.9	18.6	11.0	29.0
Phosphorus in Precipitation (kg/km^2)	32.77	3.16	8.56	3.71	3.97	9.15
Weighted concentration of Phosphorus (mg/l.)	0.032	.016	.025	.020	.036	.032
Number of Samples	98	17	34	14	4	21
Average Precipitation per Sample (cm)	1.04	1.14	1.00	1.33	2.75	1.38
Average Sample Exposure (hr)	13.1	17.6	13.3	18.3	20	24
Arithmetic Average Concentration (mg/l.)	0.043	.032	.034	.028	.034	.037
Standard Dev. of the Arithmetic Mean	0.034	.038	.024	.024	-	.024

Table 2. DISSOLVED REACTIVE PHOSPHATES IN PRECIPITATION

	DePaul Univ.	Beaver Island	Silver Lake	Illinois Beach	Rock Island	Harrison Crib
Total Precipitation (cm)	55.0	25.7	27.8	15.2	11.0	16.9
Phosphorus in Precipitation (kg/km^2)	7.57	1.53	3.88	1.50	1.23	2.30
Weighted concentration of Phosphorus (mg/l.)	.014	.006	.014	.010	.011	.014
Number of Samples	53	16	29	13	4	16
Average Precipitation per Sample (cm)	1.04	1.6	0.96	1.17	2.75	1.06
Average Sample Exposure (hr)	12.3	18.4	12.9	17.9	20.0	24.0
Arithmetic Average Concentration (mg/l.)	.018	.007	.020	.014	.012	.016
Standard Dev. of the Arithmetic Mean	.011	.005	.015	.009	-	.014

A series of rainfall samples was analyzed in order to be able to calculate how much of the phosphorus was present in the form of hydrolyzable and organic phosphates. These results are shown in Table 4. Since the analysis for hydrolyzable phosphates yields the sum of hydrolyzable plus dissolved reactive phosphates, the values shown have had the dissolved reactive phosphates subtracted out. Likewise, the organic phosphates value shown is total phosphorus minus the hydrolyzable and dissolved reactive phosphates. Values of total reactive phosphates, which are the dissolved reactive phosphates plus a portion of the hydrolyzable phosphates, are also shown.

A loading for the Lake in kilograms of phosphorus per year may be obtained by multiplying the appropriate weighted average concentration by the area of the Lake, 58,040 km^2, by the average precipitation on the Lake, 74 cm/yr (Jones and Meredith 1973) and by 10 to convert the units. This factor to convert a concentration in precipitation in mg/l. to an input in kg/yr to Lake Michigan is then 4.3×10^7.

A reasonable calculation from the data in Figure 1 would be to use the average of the DePaul and the crib data for the southern quarter of the Lake, the average of the Illinois Beach and the Silver

Table 3. TOTAL DISSOLVED PHOSPHATES IN PRECIPITATION

	DePaul Univ.	Beaver Island	Silver Lake	Illinois Beach	Rock Island	Harrison Crib
Total Precipitation (cm)	89.6	10.5	21.5	8.1	7.0	30.3
Phosphorus in Precipitation (kg/km^2)	18.4	0.97	2.54	0.99	1.05	8.37
Weighted concentration of Phosphorus (mg/1.)	.020	.009	.012	.012	.015	.027
Number of Samples	92	10	20	6	3	21
Average Precipitation per Sample (cm)	0.97	1.05	1.08	1.35	2.3	1.44
Average Sample Exposure (hr)	12.8	17.1	15.5	16.0	21.3	24.0
Arithmetic Average Concentration (mg/1.)	.025	.018	.017	.023	.016	.034
Standard Dev. of the Arithmetic Mean	.017	.012	.014	-	-	.012

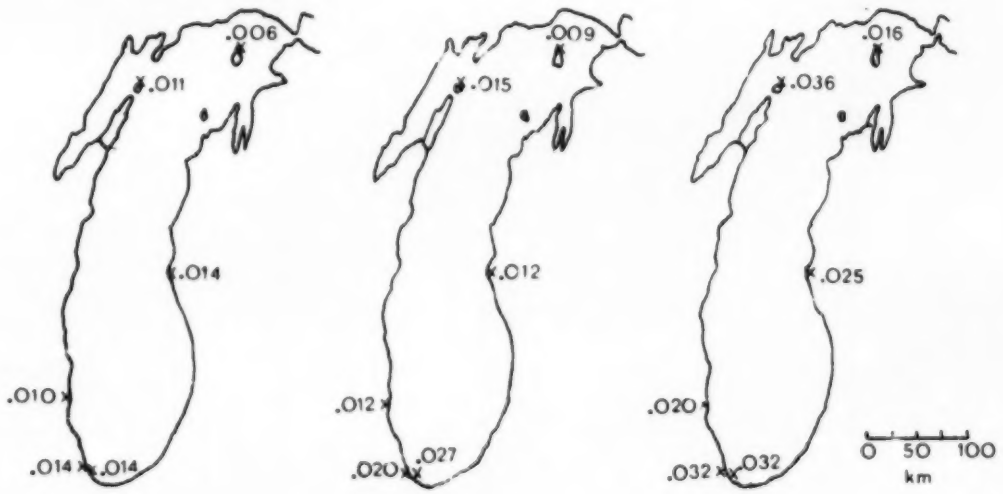
Lake data for the middle half of the Lake, and the Beaver Island data for the northern quarter of the Lake. For total phosphorus this would give an an average concentration of 0.023 mg/1. and an input of 1.0×10^6 kg/yr. For dissolved reactive phosphates, the average concentration would be 0.011 mg/1. for an input of 0.5×10^6 kg/yr.

These inputs, inputs from tributaries and direct discharges to the Lake (U. S. EPA 1974), and estimates of changes in these inputs in the future are shown in Table 5. These data indicate that about 18 percent of the phosphorus presently going into Lake Michigan is being brought in with precipitation. The program to remove 80 percent of the phosphorus from waste water discharges is now 63 percent implemented (Adamkus 1975). When it is completed, and combined sewer overflows are eliminated, inputs from precipitation could constitute about 30 percent of the phosphorus going into Lake Michigan.

The concentration of the different forms of phosphorus were also determined in the snow samples which were collected. However, principally because of the problem of accurately determining the amount of snowfall at the sampling site in Chicago due to uneven snow deposition caused by structures on the roof of the building and by the presence of adjacent

Table 4. SPECIES OF PHOSPHORUS PRESENT IN PRECIPITATION

	Dissolved Reactive	Hydrolyzable	Organic	Total Reactive
Total Precipitation (cm)	37.89	37.89	37.89	37.89
Phosphorus in Precipitation (kg/km^2)	3.79	1.65	3.29	4.68
Weighted Concentration of Phosphorus (mg/l.)	0.010	.0044	0.009	0.012
Percent of Total Phosphorus	44	19	38	53
Number of Samples	23	23	23	23
Average Precipitation per Sample (cm)	1.65	1.65	1.65	1.65
Arithmetic Average Concentration (mg/l.)	0.011	0.006	0.008	0.014



Dissolved Reactive Phosphates | Total Reactive Phosphates | Total Phosphorus

Figure 1. Precipitation weighted concentrations (mg/l.) of the forms of phosphorus in rainfall in different locations around Lake Michigan.

Table 5. ESTIMATED INPUTS OF PHOSPHORUS TO LAKE MICHIGAN

	1971[a]		December 1974[b]		Future	
	Million kg/yr	Percent	Million kg/yr	Percent	Million kg/yr	Percent
Waste Waters						
Discharges to Lake	1.7	20	0.95	17	0.35	10
Discharges to Tributaries	4.2	48	2.1	38	0.8	23
Combined Sewer Overflows	0.35	4	.15	3	--	--
Erosion	1.35	16	1.35	25	1.35	39
Precipitation[c]	1.0	12	1.0	18	1.0	29
Total	8.6		5.5		3.5	

[a]U. S. EPA (1974)
[b]Adamkus (1975)
[c]This work

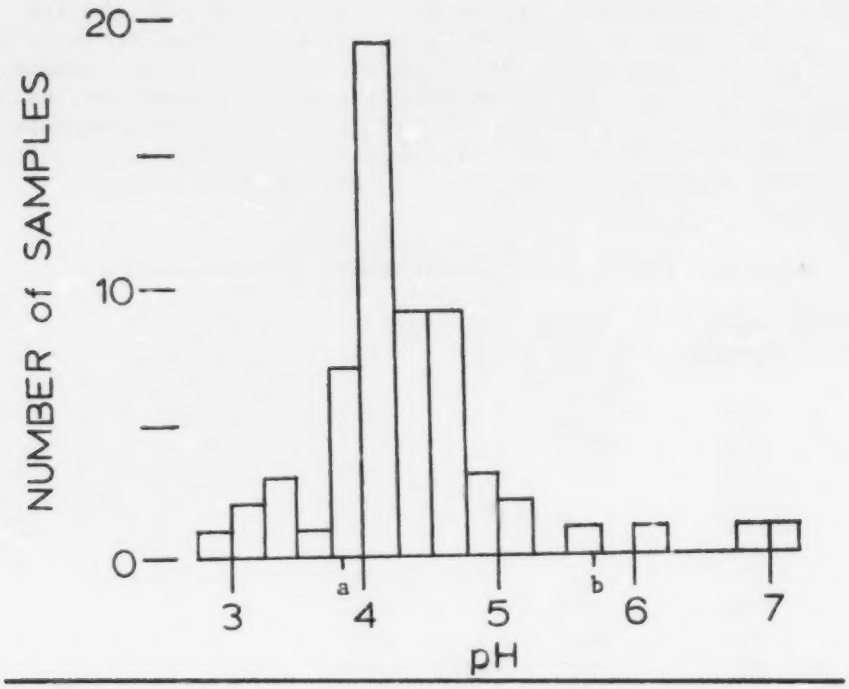
buildings of similar height, the amount of snow which fell was not measured. Thus inputs in kg/km^2 and weighted concentrations could not be determined. The concentrations found in a number of snow samples are shown in Table 6. They seem to be similar (average concentrations for DePaul samples: total phosphorus = 0.038; total reactive phosphates = 0.023) to those found in rainfall and should not significantly affect the conclusions based on the results from the rainfall samples.

Table 6. PHOSPHORUS CONCENTRATIONS IN SNOW SAMPLES

Sample Number	Phosphorus (mg/l.) Total	DRP	TRP	Collection Site
001			.041	DePaul
004	.051		.012	
012	.036		.020	
103			.026	
110			.054	
113	.034		.019	
125	.030		.017	
127	.021		.006	
128	.061		.027	
216	.016	.002	.016	
234	.054	.004	.016	
2012	.011	.004	.007	Beaver Island
2020	.007	.003		
2021	.010	.010		
2022	.012	.002	.003	
2041	.010		.010	
3001	.011	.003	.004	Silver Lake
3002		.007		
3006	.012		.007	
3007	.021		.019	
5010	.058	.024	.035	Rock Island
5011	.021	.014	.016	

The pH of 60 rainfall samples collected in Chicago over a two year period was determined. The precipitation weighted average hydrogen ion concentration corresponded to a pH of 3.85. The pH distribution of these samples is shown in Figure 2.

An unusual sample was collected on April 4, 1974. On that day a number of tornados did severe damage in Kentucky, Southern Illinois, Indiana and Ohio. At DePaul that day, 2.62 cm of rain fell. The data for this rain are shown in Table 7. Sample number 244 collected the entire rain



[a]pH corresponding to the precipitation weighted average hydrogen ion concentration, 3.85.
[b]pH of pure water in equilibrium with atmospheric carbon dioxide, 5.70.

Figure 2. Distribution of pH in precipitation samples in Chicago.

Table 7. RAINFALL ON APRIL 4, 1974

Sample Number	Hours Exposed	DRP	TRP	Total	pH
244	4	0.023	0.090	0.117	6.0
244A[a]		0.046			3.85
247	3	0.014	0.024	0.044	4.5
244-247[b]	(1)	(0.032)	(0.156)	(0.190)	

[a]Sample 244 adjusted to pH 3.85. See Text.
[b]Values in parenthesis are calculated.

event while sample number 247 collected the last 1.31 cm. That sample 247 collected exactly one-half of the rain was fortuitous.

That this was not a typical rain event was evident when sample number 244 was brought in. The bottom of the white polyethylene container was covered with a very noticable layer of reddish-brown particulate matter. Evidently the high winds associated with the storms that day were able to transport a large amount of particulate matter. Such "red rains" are infrequent but not unusual occurrences (Winchell and Miller, 1924; 1922; Robinson, 1936; Weibel et al., 1966) and cover hundreds of thousands of square kilometers. The concentration of materials in the first half of the storm, 244-247, was calculated by substracting the amounts of materials in sample 247 from the amount in sample 244 and determining the concentration for the remainder of the material. Filterable particulate matter in sample 244 was 75 mg/l. The concentrations of and the inputs from this sample are included in the data in Tables 1 to 3.

The substantial effect that each of these "red rain" events can have is illustrated by this particular storm. Of the annual precipitation inputs in the Chicago area calculated from the data in Tables 1 to 3, this one precipitation event contributed 13 percent of the total phosphorus, six percent of the dissolved reactive phosphates and 16 percent of the total reactive phosphates. In addition, 2×10^3 kg/km^2 of particulate matter was deposited.

Of more interest though are the pH and the types of phosphates in these samples. The pH of sample 244 was 6.0, quite high for precipitation samples in this area, while sample 247 had a more normal pH of 4.5. The high pH of sample 244 is attributed to the buffering by and ion-exchange with the particulate matter in the sample. While only 19.8 percent of the total phosphorus in sample 244 is dissolved reactive phosphates, 77 percent of it is total reactive phosphates. Evidently, the contact with 0.4 N sulfuric acid during the analysis, about 15 minutes, increases the amount of dissolved reactive phosphates by a factor of four! To check this effect of acid further, the following experiment was done. An aliquot of sample 244 was taken in duplicate, acidified with sulfuric acid to pH 3.8 and let stand for 30 minutes. When this treated sample, number 244A, was filtered and analyzed, the dissolved reactive phosphates concentration had doubled. Thus contact with a pH typical of rainfall for a time period typical of the lifetime of a rain droplet greatly affected the dissolved phosphates concentration in this sample.

If it is assumed that no appreciable amount of the particulate matter in sample 244 dissolved, then knowing the amount of particulate matter and of the total phosphorus present in the sample, the percent phosphorus in the particulate matter can be calculated. The results of this calculation and the results of determinations performed many years ago are shown on Table 8. Whether the present number is different from the early ones is unclear but it may be higher due to the heavier use of phosphorus containing fertilizers in recent years.

Table 8. PERCENT TOTAL PHOSPHORUS IN PARTICULATE MATTER FROM "RED RAINS"

Date	Total Phosphate
4 April 1974	0.15%
13 February 1923[a]	0.07%
19 March 1920[b]	0.06%

[a]Winchell and Miller, 1924.
[b]Winchell and Miller, 1922.

To check on the possible interference of arsenate, AsO_4^{3-}, in the phosphorus analysis, the concentration of arsenate was determined in 24 samples. Seventeen of these were from DePaul and seven were from other locations around the Lake. The average concentration found (3.75 ±3.6 ppb As) corresponds to a phosphorus concentration of 1.55 ppb with a standard deviation of 1.49 ppb. The intensity of the color of the complex with the arsenate developes more slowly than that from the phosphate, therefore, only about two-thirds of the arsenate present would appear as phosphate. Since the arsenate correction was low, it was less than other variables in these determinations, and because other reported values for phosphorus are not corrected, the phosphorus values reported here are also not corrected.

Five precipitation samples were collected in conjunction with high volume air particulate samples. Each was analyzed for total phosphorus and dissolved reactive phosphates and the concentrations of these determined in the rain and in the air. These concentrations and the washout ratio calculated from them are shown in Table 9. The ratio for the total phosphorus and the dissolved reactive phosphates may be different, indicating that, at least partially, these have different sources. The washout ratio indicates an average particle diameter of about three microns (Gatz, 1973).

Table 9. WASHOUT RATIO

Phosphorus Concentration

Sample Number	Precipitation (ug/l.)		Atmosphere (ug/m^3)		Washout Ratio[a]	
	DRP	Total	DRP	Total	DRP	Total
142	7.5	12	0.037[b]	0.066[b]	261	234
220	15	25	0.022	0.067	879	1040
297	11	29	0.030	0.055	473	680
298	12	56	0.050	0.110	310	656
299	19	43	0.062	0.102	395	543
average					464	631

[a] = (ug/kg in precipitation)(ug/kg in atmosphere)
= 1.29 x (ug/l.)/(ug/m^3)

[b] Geometric mean of 25 samples from City of Chicago network.

Four glacial samples were available for analysis. Three were of sections of cores melted at the time of collection and stored as water in polyethylene containers. The last sample, number 81, was stored as a frozen core until a portion was taken and thawed into a clean glass container for this project. Upon reaction with the combined reagent for the phosphorus analysis, two of the samples had an absorption at 750 nm which interfered with the analytical absorption peak at 880 nm. The results obtained from the other two glacial samples are shown in Table 10.

Table 10. PHOSPHORUS IN GLACIAL SAMPLES

Year of Deposition	DRP (mg/l.)	Total Phosphorus (mg/l.)
1650	0.0015	0.0024
1966-7	0.0017	

To check on the precision and accuracy of the analyses, two things were done. First, the results from the analysis of the 0.010 mg/l. phosphorus standard on 100 different occasions showed an average concentration of 0.00976 mg/l. phosphorus with a standard deviation of 0.00096 mg/l. Secondly, a group of samples containing three different levels of phosphorus were analyzed as part of a laboratory intercomparison study by

the Upper Lakes Reference Group. All of our results were well within one standard deviation of the group averages.

On several occasions, multiple samplers were exposed to check the variability in samples collected at one site from the same rain event. For six different events and a total of 17 different collectors, the average variation from the mean was 16% for total phosphorus, 11% for dissolved reactive phosphates and 6.5% for total reactive phosphates. For the dissolved reactive and total reactive phosphates samples, much of the variability noted is probably due to variability in sub sampling and in the analyses. All of the percentages are well below that found for the variability between individual precipitation events.

Since it was not expected that all precipitation events would be sampled, the samples came in with some degree of irregularity from all of the sites. The total number of samples obtained was: 191 from DePaul; 41 from Beaver Island; 52 from Silver Lake State Park; 21 from Illinois Beach State Park; 11 from Rock Island State Park and 120 from the Harrison Crib. For the reasons to be discussed, not all of these samples were able to be used for the final calculations.

SECTION VI

DISCUSSION

The results shown in Tables 1, 2 and 3 and in Figure 1 are based on the samples collected in this project. However, not all of the samples collected were analyzed nor were the results of all of the samples analyzed used in the calculations. Samples, or the results from samples, were rejected for the following reasons:

1) The collection container was exposed for more than 24 hours
2) The sample contained insects, leaves or a large amount of particulate matter.
3) The total phosphorus concentration of a sample from an event of more than one centimeter of precipitation was higher than 0.100 mg/1. and there was no reason to suspect that the sample was not contaminated in some way.

The largest number of samples and the most conplete set of data were obtained in Chicago at the DePaul site. It was anticipated that the greater concentration of particulate matter in the atmosphere in the urban area would lead to an increase in the phosphorus concentration of the samples collected in Chicago (Murphy 1974). Such an effect was found, but it is not as large as expected. One reason for the effect being small may be that the collecter was more than fifteen meters above the ground and thus above much of the traffic related particulate matter.

The site at the Harrison crib in Chicago was chosen to try and correct for some of the effects of the urban area. The results obtained were very different from those expected and can only be partially explained.

On the crib, the sample containers were almost without exception, changed at 8 a.m. Thus these are all 24 hour samples. It was surprising how much particulate matter was in many of the samples. It seemed to be much more than that obtained in 24 hour samples from any of the other locations. In fact, more than 80 percent of the crib samples or the results from these samples, were rejected because of the large amount of particulate matter or insects in the samples, or because the analytical results were very high. For example, 14 of 40 samples (35%) from the crib analyzed for total phosphorus had concentrations higher than 0.100 mg/1. while only four of more than 200 of the samples collected at DePaul (2%) had such high concentrations. About half of the high crib samples, and only one of those collected at DePaul, occurred with precipitation events of more than one centimeter of rain. It is not clear why the crib samples contained so much particulate matter.

A problem of unforeseen magnitude on our part was that of insects. It turns out that the crib, about 4 kilometers from shore is a mecca for insects, many of which end up in the collecters. The men on the crib confirmed that insects were a great nuisance during warm weather.

The variability of the concentration of phosphorus between different rainfall events is high. Thus one must obtain a number of samples in order to get a good estimate of what the average concentration might be. This is probably the reason the average value of the total phosphorus concentration for the Rock Island samples (0.036 mg/l.) is higher than expected. It is based on only four samples. It can be seen in Tables 1, 2 and 3 that the standard deviation of the arithmetic average concentration is almost as high as the average itself in most cases.

Another variable which must be kept in mind is the fact that the concentration of phosphorus generally decreases as the amount of precipitation in an event increases. An illustration of this variability in concentration and thus in phosphorus input, is shown in Figure 3. This figure is a plot of the inputs of phosphorus from each of the samples of total phosphorus and DRP used in the calculations shown in Tables 1 and 2, versus the amount of precipitation each sample represented. Also shown in Figure 3 are iso-concentration lines which show, for any amount of precipitation, the concentration of phosphorus which would give the indicated input. It can be seen clearly that smaller amounts of precipitation have higher concentrations of phosphorus. This means that the small precipitation events contribute a higher proportion of the phosphorus than their amount of precipitation would indicate. This is why a precipitation weighted average concentration is lower than an arithmetic average concentration and why one must try to obtain a representative sample of rainfall events of different amounts of precipitation and from different types of storms.

It is also generally true that the early precipitation in an event will be more concentrated than the later precipitation. The reasons for this are varied and have been discussed by Gatz and Dingle (1971). Thus it is important to have the collector out and open at the beginning of each event.

One of the important goals of this project was to contribute information on the species of the phosphorus present in the precipitation and therefore on how significant these inputs might be to the Lake. The results in Table 4 show that 43% of the phosphorus in precipitation is dissolved reactive phosphates. This along with the information in Table 5 that 18% of the phosphorus presently going into Lake Michigan is coming from the precipitation in the atmosphere, indicates that these inputs are an important part of the phosphorus budget of the Lake. The magnitude of these inputs and the fact that they are an uncontrollable source will have to be taken into account when the present phosphorus control programs are evaluated and when new ones are considered. It should also be remembered that dry deposition is also contributing phosphorus to the Lake and that the phosphorus inputs from tributary streams contain a lower percentage of DRP.

The observation of the difference between the dissolved reactive phosphates and the total reactive phosphates determination, and of the results of the pH changes on the concentration of DRP in sample number 244 indicate

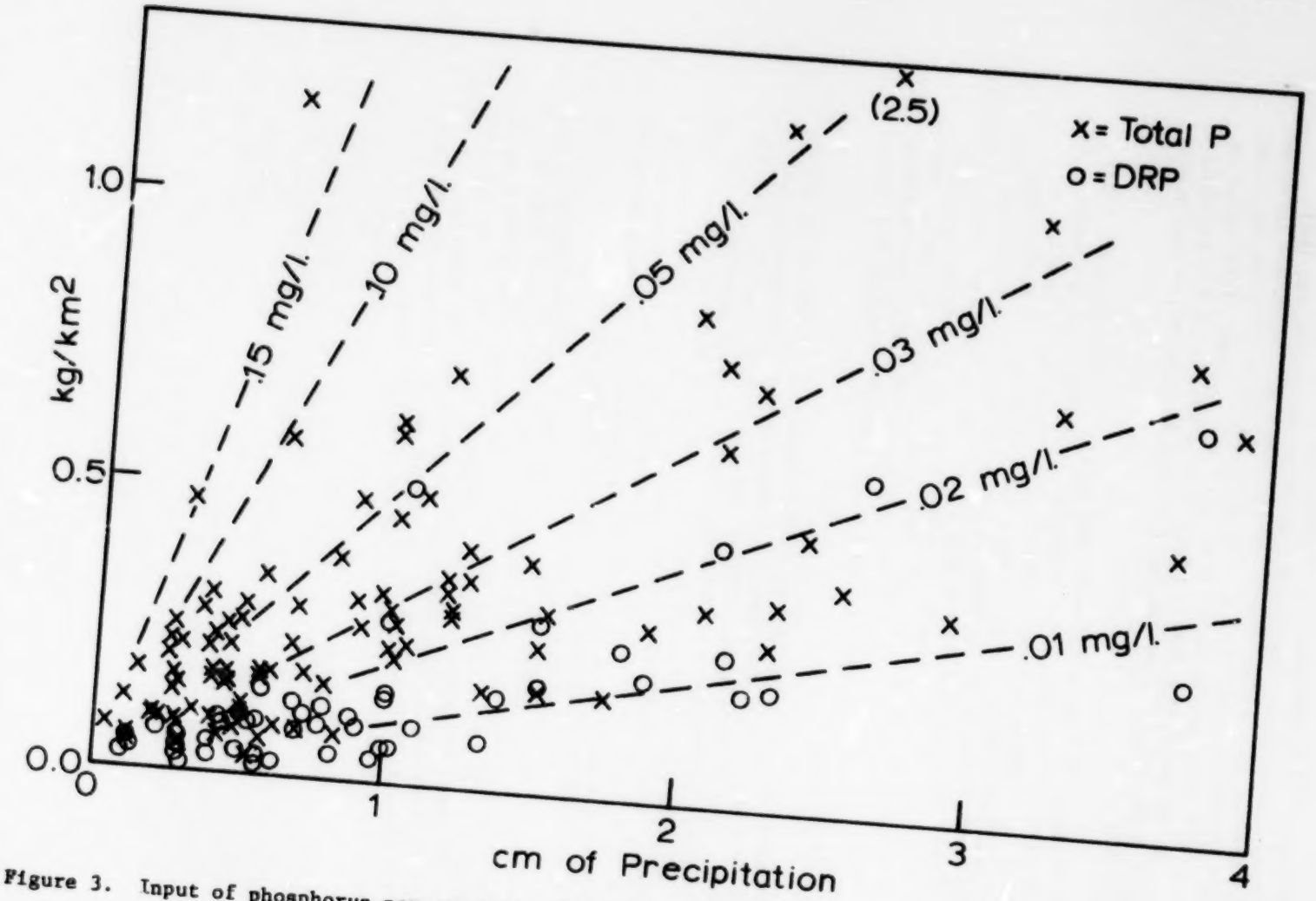


Figure 3. Input of phosphorus per precipitation event.

that the amount of DRP determined is a function of the pH of the sample at the time of filtration. Therefore, in order to obtain the most meaningful results, the sample should be filtered at a standard pH value. Whether this should be a pH of 8.0, the approximate acidity of the Lake, a pH of 4.0, the approximate acidity of rainfall or some other value is not clear. It is not known what happens to the DRP in pH 4.0 rainfall when it enters the Lake. That is, is it taken up by particulate matter or by organisms.

The ready release of some additional DRP by the acidic rainfall indicated that some of the adsorbed phosphorus is readily exchangeable. How much of this ultimately becomes available in the Lake? Ideally, a bioassay on precipitation samples would give this information. The difficulty with doing this, however, is the variability in the results when bioassays are performed on samples with low phosphorus concentrations. Attempts were made with a number of samples to use the anion exchange method of Cowen (1974), but we were unable to obtain consistent, reproducable results. It was also not obvious to us that the ion-exchange resin would successfully compete with the organisms present for all of the ortho phosphate.

The next best method is to try to find a chemical determination which would give a measure of the amount of phosphorus in the sample that ultimately becomes available. Walton and Lee (1972), report that the total reactive phosphates determination gives a good measure of the amount of phosphate which ultimately becomes available in Lakes Mendota and Wingra. A more conservative estimate would be the DRP at rainfall acidity. The most conservative estimate would be the DRP determined on a sample filtered at Lake water acidity while the maximum would be the DRP plus the hydrolyzable and organic phosphorus.

The data in Table 4 permit estimates using the different assumptions, with the exception of the dissolved reactive phosphates at Lake pH, to be compared. It is felt that the dissolved reactive phosphates plus some additional phosphorus becomes available to organisms in the Lake. Therefore, with all of the variables in precipitation sampling, it is felt that an estimate of 50% of the total phosphorus may be the best estimate of the available phosphorus in precipitation.

SECTION VII

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